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MICROBIOLOGICAL TREATMENT OF ACID MINE DRAINAGE LABORATORY AND FIELD STUDY UPDATE

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ABSTRACT

A laboratory model continuous treatment system has been run for more than fourteen months resulting in a change in pH from 3.5 to generally greater than 6.0. Concurrently there have been substantial reductions in both the iron and sulphate content of the simulated acidic drainage during treatment. Greater than 99% removal of aluminum has been observed. When the laboratory model was scaled up 550 fold for a field test results similar to the laboratory tests where observed until mid-July, 1990, at which time the anaerobic zone which had developed in the system was severely disturbed while adding fresh straw to the system. The system took about 8 weeks to re-equilibrate, and is currently showing complete removal of aluminum with an average effluent pH of greater than 4.5.

INTRODUCTION

Acid mine drainage (AMD) is considered to be the largest single environmental problem facing the mineral industry today (Filion and Ferguson, 1990). AMD is characterized by a low pH, a high sulphate content, and the presence of dissolved metals such as iron or aluminum. The widespread use of liming to treat AMD is no longer considered acceptable in the long term and new treatment processes are sought to neutralize the pH and reduce its metal content to meet environmental regulations.

Sulphate-reducing bacteria (SRB's) participate in AMD mitigation (Tuttle et al., 1969a; Mills et al., 1989). Mitigation of AMD was reported after passage through a wood dust dam (Tuttle et al., 1969b), straw (Kalin, 1989), peat (Eger and Lapakko, 1988), hay (Stark et al., 1988) and mushroom compost (McIntire and Edenborn, 1990). Degradation of the organic matter probably led to the establishment of anaerobic conditions within the substrate and generated nutrients for the SRB's, which then reduced the sulphate present in AMD into hydrogen sulphide. The H_2S thus produced could precipitate with metallic ions in solution. Other microorganisms are also implicated in AMD mitigation (Mills et al., 1989).

Tuttle et al. (1969b) suggested using SRB's to treat AMD in the presence of wood waste and Wakao et al. (1979) studied the continuous small-scale neutralization of AMD using mixed cultures containing SRB's. Recently, some authors using wetlands and/or ecological engineering to treat AMD have looked at stimulating sulphate-reduction as a means of optimizing the mitigation process (Kalin, 1989; McIntire et Edenborn, 1990).

The main objective of this project is to develop a commercially viable process to treat AMD using microbial populations including SRB's in the presence of cellulosic material. A pilot-scale model was set up in the laboratory to treat artificial AMD (Béchard et al., 1990a). Results obtained during a period of maintenance that has lasted for over a year are

presented. In addition, field testing was started in August 1989 at Halifax International Airport (Béchard et al., 1990a). Results collected during the 1990 summer season are discussed.

MATERIAL AND METHODS

Treatment of artificial AMD

The setup of the pilot-scale model was described previously (Béchard et al., 1990a, 1990b). Straw and wood shavings were used as a source of cellulose. The artificial acid water used in this study starting August 1989 was (in mg/L): $MgSO_4.7H_2O$, 1667; $FeSO_4.7H_2O$, 500; dextrose, 1000; urea, 100; K_2HPO_4, 27. This corresponds to an iron concentration of 100 ppm, sulphate concentration of 1000 ppm, and phosphate concentration of 15 ppm. Starting September 1st, the dextrose concentration was reduced to 500 mg/L and that of urea to 50 mg/L; starting September 15, the $FeSO_4.7H_2O$ concentration was increased to 1000mg/L (200 ppm of iron) and that of $MgSO_4.7H_2O$ decreased to 556mg/L; starting January 2nd, 1990, the dextrose concentration was decreased to 400 mg/L, and that of urea to 40 mg/L; starting March 1st, 1990, the dextrose concentration was again lowered to 200 mg/L; starting March 29, 1990 the $MgSO_4.7H_2O$ concentration was lowered to 31 mg/L and sulphate was supplied mainly as Na_2SO_4, 2192 mg/L; starting April 9, the Na_2SO_4 concentration was reduced to 950 mg/L in order to get a 1000ppm final sulphate concentration, and dextrose was replaced with sucrose 200 mg/L; starting June 8, the sucrose concentration was increased to 300 mg/L; starting June 14, 25ppm aluminum as $Al_2(SO_4)_3$ 286 mg/L was added; starting July 12, the $Al_2(SO_4)_3$ concentration was increased to 813 mg/L and the Na_2SO_4 decreased to 580 mg/L; starting August 13, the $Al_2(SO_4)_3$ concentration was restored to 286 mg/L and that of Na_2SO_4 to 950 mg/L. Concentrated sulphuric acid was used to adjust the pH to 3.5. Straw in the 2nd trough from the top was completely replaced with fresh straw on

August 4, 1989 and on August 23, 1990. Some straw from the 3rd trough from the top was replaced on September 11, 1990. The flow rate was maintained at 23 mL/min.

Halifax test cells

Start-up of the field test at Halifax International Airport was described previously (Béchard et al., 1990a, 1990b). In the spring, work was done on the clay lining of the cells to repair damage done during the winter by freezing and thawing. Straw and swamp mud were mixed thoroughly into the biomass contained in all three cells on July 13, 1990. Straw was also added to the top of the three cells on September 7, 1990. Sugar and urea were added to the system during the month of June. Straw containing SRB's from the laboratory troughs, sugar and urea were added to the cells on August 27, 1990.

Chemical and physical water analyses

For the pilot-scale testing, chemical analyses for pH, sulphate and iron were done at CANMET as described previously (Béchard et al., 1990a). Starting June 1990, iron, aluminum and phosphorus concentrations were determined by inductively coupled plasma sequential spectroscopy using a Jobin-Yvon model 38 (Longiumeau, France).

Flow rate within the pilot-scale model was measured by collecting effluent in a graduated cylinder for a five-minute period using a digital timer, and repeating once.

At the Halifax field test site, water samples were taken weekly at 4 sampling sites. Water temperature, flow rate and pH were measured in the field (Béchard et al., 1990a). Starting May 1990, the pH was measured using a portable pH-meter. Determination of pH, iron, aluminum, acidity, total dissolved solids, ammonia, nitrate and nitrite, phosphorus, sulphate and total organic carbon was done at the Laboratory of Fnvironmental Chemistry, Division of Clinical Chemistry, Victoria General Hospital, Halifax.

Precipitate analysis

Samples of the black precipitate within the pilot-scale model were taken in March in an area where there was no straw, and in August 1990 from deep within the organic material. They were dried and analyzed by x-ray diffraction for sulphur, aluminum and iron sulphides. The samples were ground by hand with a mortar and pestle and this "bulk" fraction was scanned from 15° to 90° teta on a Rigaku automated powder diffractometer. Scan conditions were as follows: 55kv, 180 mA, 10° per minute scan speed and a 0.05° sample interval.

Microbial analyses

Once a month, biomass samples were taken at every 1/3 and 2/3 of each cell (2 samples/cell) and sent to CANMET for analysis. Total fungal counts, total aerobic heterotrophic bacterial counts and sulphate-reducing bacterial counts were performed as described previously (Béchard et al., 1990a).

RESULTS

Pilot-scale model

Results are presented for artificial AMD treated by the system since water of pH 3.5 has been used. Figure 1 presents pH measurements taken from the beginning of August 1989 to the end of October, 1990. The pH of the effluent is consistently higher than 6.0. Lower effluent pH's were measured when the sugar concentration was lowered in March and when the aluminum concentration was tripled in June. Iron removal from artificial AMD treated by the pilot-scale system from August 1989 to September 1990 is presented in Figure 2. During the first 6 months, virtually no iron was found in the effluent. When the sugar concentration was lowered in March and when aluminum was added to the artificial AMD from June onwards, less than 70% of the iron was

eliminated. Residual iron exits the system as ferrous iron. Aluminum was completely eliminated from artificial AMD at both average and high concentrations (Figure 3) over a period of four months.

X-ray diffraction analysis of the trough precipitate revealed that the March sample contained elemental sulphur and greigite (Fe_3S_4). The August sample contained elemental sulphur, greigite, pyrite (FeS_2) and an unidentified product. No aluminum was detected.

Halifax field test

The results presented in this section were obtained during the first summer of this field study, from April to October 1990. Figure 4 presents pH measurements taken in the field for water entering and exiting the three cells. Up until July 13, although the pH of the influent was continuously changing, effluent pH was consistently equal to or greater than 6. The pH of the water increased steadily as it flowed through each of the cells. For example, on July 10, 1990 influent pH was 3.65; the pH measured between cell #1 and cell #2 was 4.80, that measured between cell #2 and cell #3 was 5.24 and the pH of the effluent was 5.95. From July 13 onward, the pH of the effluent was no longer greater than 6. An important increase in pH was only measured on September 5, and on sampling dates after October 26 (data not shown).

Aluminum was very effectively removed from the AMD up till July 13 (Figure 5). The concentration of aluminum in the water decreased steadily as it flowed through the three cells, with in most cases more than half of the aluminum being eliminated in the first cell. Aluminum was no longer effectively removed after July 13, and at times the effluent contained greater amounts of aluminum than the influent.

Initially, iron was effectively removed from the system (Figure 6). Throughout the month of June, the amount of iron found in the AMD increased dramatically after passage through the first cell before decreasing. After July 13, iron was no longer

effectively removed and at times the effluent contained greater amounts of iron than the influent. A great deal of iron oxide precipitate accumulated in the pond located before the first cell.

The percentage of sulphate removed from the AMD is shown in Figure 7. Over 50% of the sulphate was generally removed from the AMD up till July 13. Afterwards, in several instances sulphate was generated as the AMD flowed through the cells. A strong sulphide smell for the water flowing through the cells was reported throughout the spring, at the beginning of September, and again in November.

Figure 8 gives an estimate of the number of sulphate-reducing bacteria present 1/3 downstream from the beginning of each cell. These microorganisms were generally present in the 10^4 cells/mL range. The numbers were slightly lower in the October samples.

The water temperature stayed very cool (less than 10°C) till the week of June 18. Flow rates remained generally slower than 15 L/min. throughout most of the summer. There were heavy rainstorms in September and October, with flows going in at up to 75 L/min. on one occasion. During the summer, swamp grass that had been seeded the previous fall grew around the cells, and a small bush was found at the beginning of cell #2. When the site was inspected on August 27, the level of water in the cells was very low. Some of the pipes which allow the water to flow from one cell to another were dry, and the flow rate at the end of the third cell was less than 1 L/min. The three pipes which allow water from the pond to flow into the first cell were found to be coated with a thick iron oxide precipitate, which was quickly removed with a shovel. Three hours later, the flow rate was up to 10L/min. and still increasing. The water flowing through the biomass was orangy/brown, whereas that flowing through the system when it was operating properly was black. In addition, although the straw in the last two cells was packed so that straw covered the water level, the straw in the first cell was saturated with AMD.

DISCUSSION

The laboratory model used to treat artificial AMD of pH 3.5 has successfully been running for 14 months. The pH of the effluent has at all times been higher than 6, thus meeting the recommended guidelines for mining effluents (Anonymous, 1987a). Dextrose seems to enhance the process in the pilot-scale model, as discussed previously (Béchard et al., 1990b).

Dextrose was substituted quite readily by sucrose, a form of sugar that is widespread in nature. In a previous paper, it was reported that a significant reduction in the amount of sulphate and iron removed from the influent after passage through the troughs was obtained when using only 200 mg/L of sugar. Because the expected increase in the microbial activity observed within the troughs did not occur, the sugar content of the artificial AMD was increased to 300 mg/L. Ideally, we hope to eliminate the need for sugar addition. It may prove necessary to incorporate a small amount of carbohydrates into the straw and wood waste within the optimized process. The first part of the laboratory study, setting up a pilot-scale model which could treat AMD continuously for a long period of time, is completed.

The iron present in the artificial AMD was removed essentially as iron sulphides, as shown by the x-ray diffraction analysis of the precipitate formed within the troughs. The formation of metal sulphides was reviewed by Krouse and McCready (1979). The H_2S produced by the SRB's ionizes in aqueous solutions to form S^{2-}, which can react with ferrous ions to yield amorphous ferrous sulphide FeS. The initial iron precipitate is thought to be poorly crystallized mackinawite, $FeS_{0.94}$ (Ward, 1970). The sulphide present in the system can also be oxidized to form elemental sulphur. When limited oxygen is available, the iron sulphide will by subsequent sulphurisation reactions yield pyrrhotite ($FeS_{1.1}$), greigite and pyrite. As sulphurisation prceeds, the precipitate becomes more and more stable under anaerobic conditions. Finding greigite and

pyrite in the system is important, as it confirms that we are trapping the iron in an insoluble form that will remain stable as long as the system remains anaerobic. In fact, since AMD is most commonly produced from pyrite, we are in essence transforming the AMD back to what we had initially. No mackinawite was found in system, suggesting that either it is rapidly transformed into the more stable greigite, or that the formation of greigite is done using another sequence of reactions. In fact, an unidentified product was present in the precipitate. To the best of our knowledge, none of the authors that have studied the use of SRB's to treat AMD have analyzed the precipitate formed within their system.

Aluminum was not found in the precipitate analyzed. Since aluminum was added to the artificial AMD starting in June, the amount of aluminum accumulated within the precipitate may not have been high enough to detect it. Aluminum may also have been present in the unidentified product, or elsewhere in the system. Since all of the aluminum is trapped within the system, further analyses will be conducted to determine where and how it is being removed.

When aluminum was added to the artificial AMD, and in particular when the concentration was tripled to 75 mg/L, an immediate effect was seen on the effluent pH and on the amount of iron effectively removed from the system. The toxicity of aluminum Al^{3+} usually results from inhibition of Mg^{2+}-dependent enzymes (Hughes and Poole, 1989). It will be interesting to verify whether increasing the magnesium concentration in the artificial AMD will help alleviate this toxicity.

Results from the field test were very promising until July 13. Parameters, such as pH and aluminum, measured in the effluent met the effluent requirements set for Halifax Airport (Anonymous, 1987b).

Problems were encountered when straw was improperly added to the system. When the material was mixed in, oxygen was incorporated throughout the cells, thus disrupting the ecosystem

that had evolved within the organic material since start-up in August 1989. Instead of mitigating AMD, the cells at some point oxidized sulphate and iron and resolubilized aluminum. Since SRB's do not grow in the presence of oxygen, it is vital that part of the system be kept anaerobic if mitigation of AMD is to occur.

When this problem was discovered in August 1990, material from the pilot-scale model as a source of inoculum, sugar, urea and straw was added to the system to recreate a good environment for microbial activity. Recent results have shown that the system is working again. Although microbial mitigation will be disrupted by incorporating massive amounts of oxygen, activity can be restored.

One year after start-up, iron oxides are starting to fill up the pond located just before the first cell. This orange precipitate must be pumped out, and subsequent designs will have to take this into account.

New treatment technologies are urgently needed for acid mine drainage. Microbial mitigation of acid water using cellulosic materials is a potentially effective treatment. Further experiments in the laboratory should enable us to optimize the microbial activities involved. The first summer of the field test has been successful, in spite of the problems encountered. Additional results from the field test should confirm that the process developed is effective in treating AMD to meet effluent requirements.

ACKNOWLEDGMENTS

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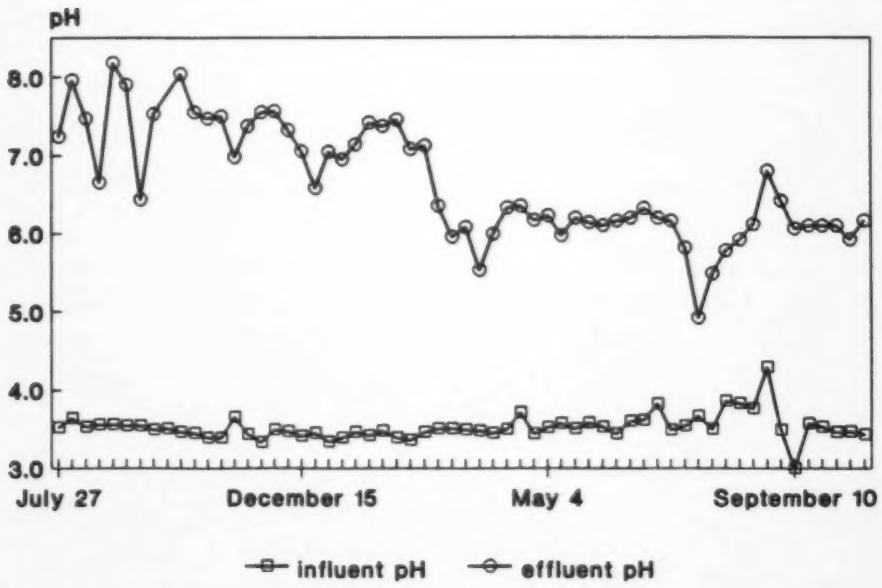

Figure 1 Neutralization of Artificial AMD, 1989-90

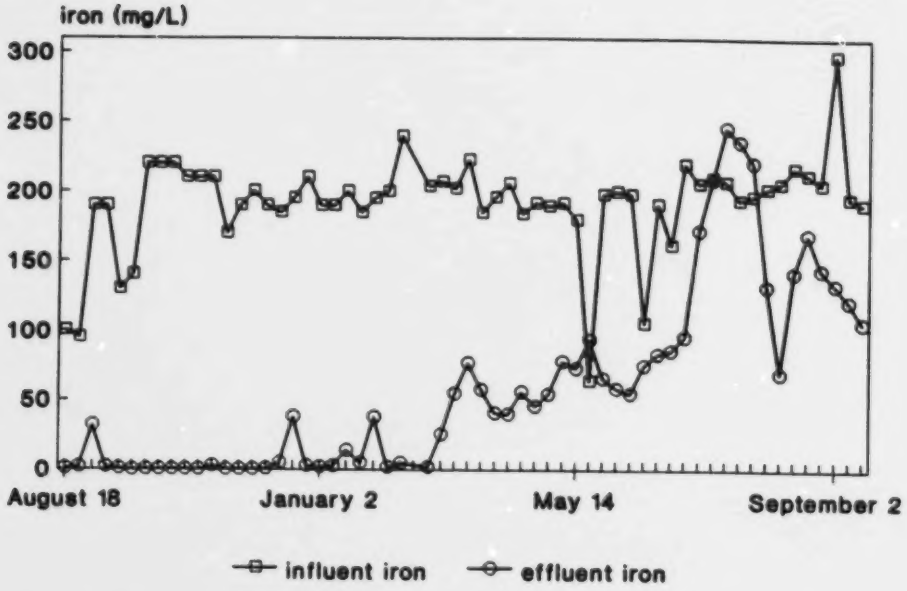

Figure 2 Removal of Iron from Artificial AMD, 1989-90

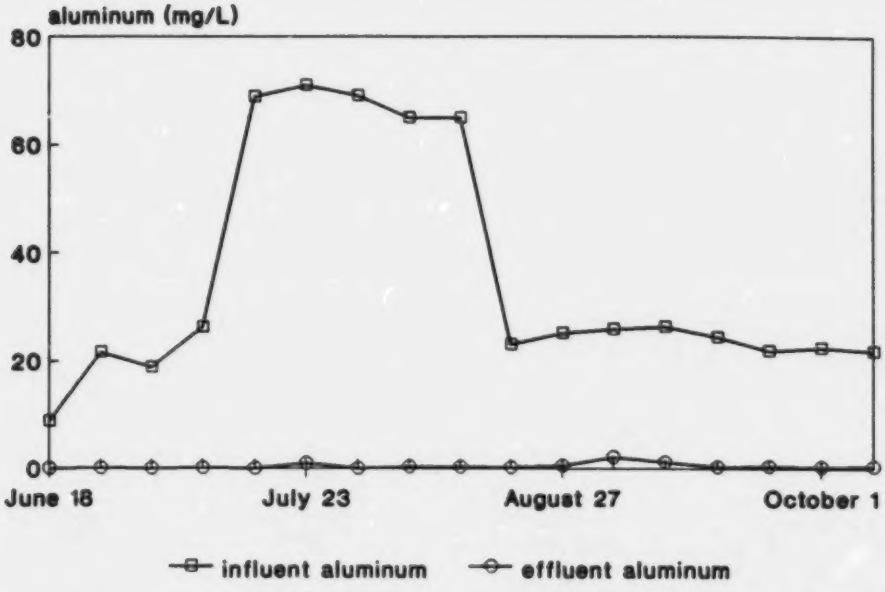

Figure 3 Removal of Aluminum from Artificial AMD, 1990

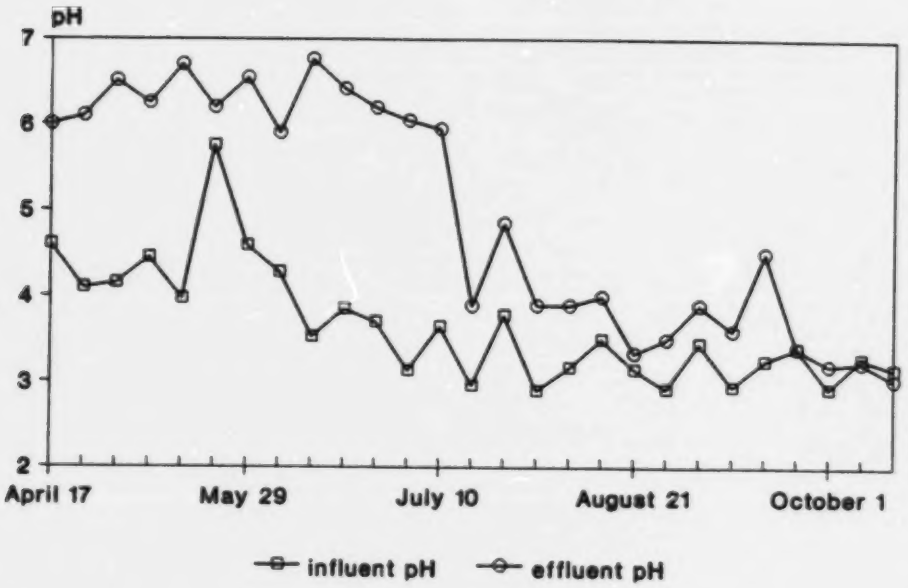

Figure 4 Neutralization of AMD at Halifax Airport, 1990

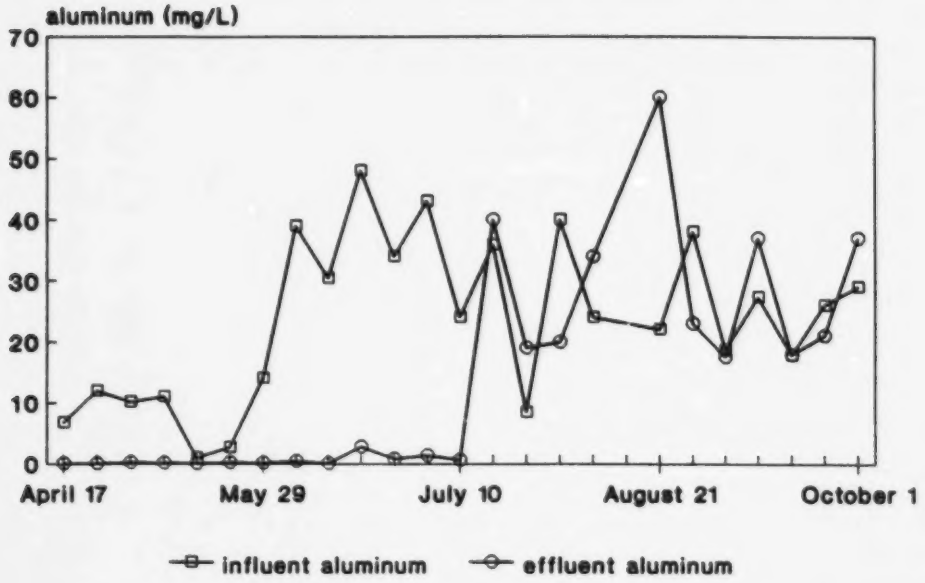

Figure 5 Removal of Aluminum at Halifax Airport, 1990

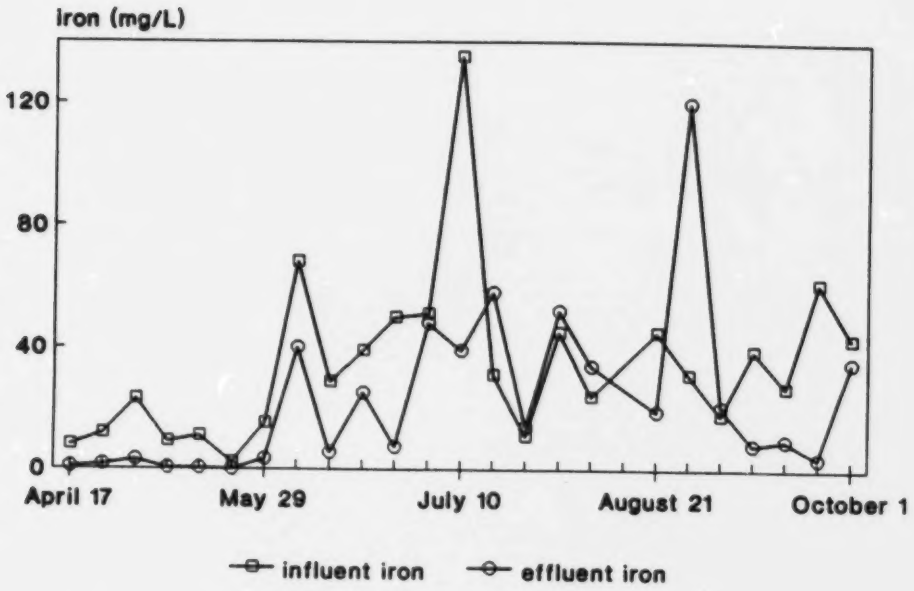

Figure 6 Removal of Iron at Halifax Airport, 1990

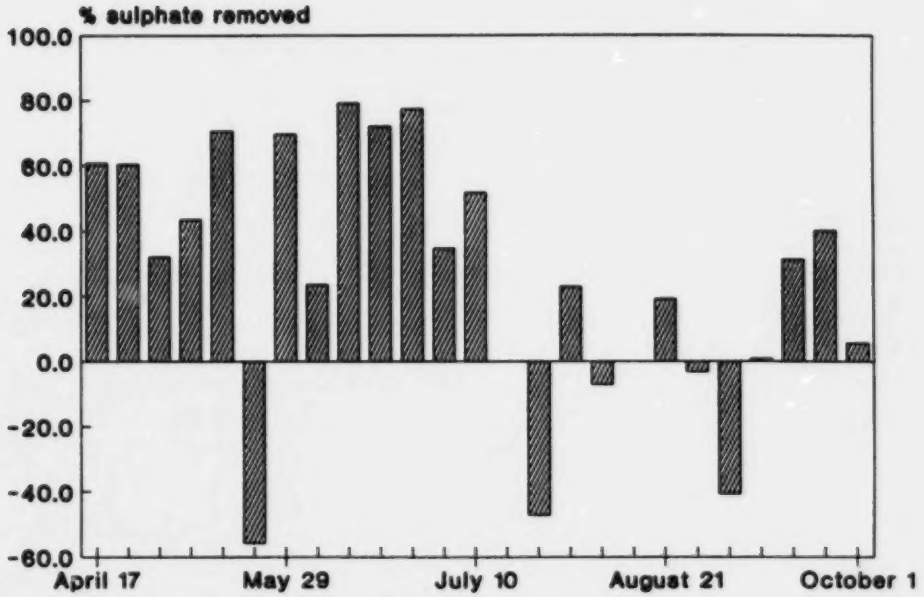

Figure 7 Removal of Sulphate at Halifax Airport, 1990

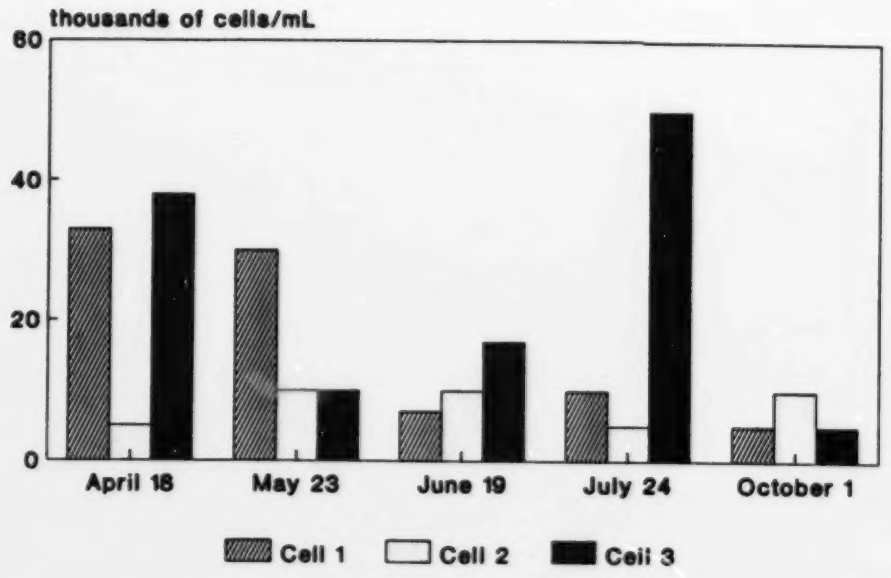

Figure 8 Sulphate-Reducers in Biomass Samples, 1990